

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188		
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) 16-10-2012		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 29-Jun-2009 - 28-Jun-2012	
4. TITLE AND SUBTITLE Carbon Single Walled Nanotubes- Electron Acceptor Molecules for Improving the Efficiency of the Photoexcitation of TiO2 for Solar-Driven Technologies			5a. CONTRACT NUMBER W911NF-09-1-0371		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER 611102		
6. AUTHORS John T. Yates, Jr.			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Virginia Office of Sponsored Programs The Rector and Visitors of the University of Virginia Charlottesville, VA 22904 -4195			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSOR/MONITOR'S ACRONYM(S) ARO		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) 55748-CH.12		
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT Photoluminescence (PL) spectroscopy and infrared(IR)spectroscopy have been used to measure the surface condition of TiO2 powder. The adsorption of electron acceptor and donor molecules has been shown to modify band bending at the TiO2 surface. Single walled nanotubes (SWNTs) are shown to be electron acceptor molecules. The PL was used to observe the buildup during UV irradiation of surface photovoltage, and it was found that TiO2 particles, fused and pressed together by water treatment + drying, led to enhanced interparticle conductivity					
15. SUBJECT TERMS TiO2; Single Wall Nanotubes, Photovoltaic Cells, Electron Acceptor Molecules, Photoluminescence					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON John Yates
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 434-924-7514

## Report Title

Carbon Single Walled Nanotubes- Electron Acceptor Molecules for Improving the Efficiency of the Photoexcitation of TiO<sub>2</sub> for Solar-Driven Technologies

### ABSTRACT

Photoluminescence (PL) spectroscopy and infrared (IR) spectroscopy have been used to measure the surface condition of TiO<sub>2</sub> powder. The adsorption of electron acceptor and donor molecules has been shown to modify band bending at the TiO<sub>2</sub> surface. Single walled nanotubes (SWNTs) are shown to be electron acceptor molecules. The PL was used to observe the buildup during UV irradiation of surface photovoltage, and it was found that TiO<sub>2</sub> particles, fused and pressed together by water treatment + drying, led to enhanced interparticle conductivity compared to TiO<sub>2</sub> particles pressed in a dry condition and considered to be isolated. The conductivity can be used to monitor conduction through the TiO<sub>2</sub> bed and through the bed containing SWNT linkers. It was found that while SWNTs are good acceptors, no added conductivity from isolated TiO<sub>2</sub> grain to grain was seen even for 10% mixtures. It was shown that PL gives insight into the electronic state of the very outermost TiO<sub>2</sub> particles in a packed bed. Such beds are used in photovoltaic cells. The PL-IR spectrometer is unique in the field, allowing both chemical and electronic properties to be measured for the surfaces of small semiconductor particles.

---

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

#### (a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2012/10/16 11	Michael Büttner, Zhen Zhang, Ana Stevanovic, John T. Yates. Photoluminescence of TiO <sub>2</sub> : Effect of UV Light and Adsorbed Molecules on Surface Band Structure, Journal of the American Chemical Society, (01 2012): 0. doi: 10.1021/ja2072737
2012/10/15 8	Hannu Häkkinen. The gold-sulfur interface at the nanoscale, Nature Chemistry, (05 2012): 0. doi: 10.1038/nchem.1352
2012/10/15 9	Zhen Zhang, John T. Yates. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces, Chemical Reviews, (10 2012): 0. doi: 10.1021/cr3000626
2012/10/15 10	John T. Yates. Electron stimulated desorption, DIET, and photochemistry at surfaces: A personal recollection, The Journal of Chemical Physics, ( 2012): 0. doi: 10.1063/1.4746798
2012/10/15 6	Oleksandr Voznyy, Jan J. Dubowski, J. T. Yates, Peter Maksymovych. The Role of Gold Adatoms and Stereochemistry in Self-Assembly of Methylthiolate on Au(111), Journal of the American Chemical Society, (09 2009): 0. doi: 10.1021/ja902629y
2012/10/15 7	Ana Stevanovic, John T. Yates. Probe of NH <sub>3</sub> and CO Adsorption on the Very Outermost Surface of a Porous TiO <sub>2</sub> Adsorbent Using Photoluminescence Spectroscopy, Langmuir, (04 2012): 0. doi: 10.1021/la205032j

**TOTAL: 6**

**Number of Papers published in peer-reviewed journals:**

---

#### (b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
2011/08/11 11 3	John T. Yates, Zhen Zhang. Electron-Mediated CO Oxidation on the TiO, Journal of the American Chemical Society, (09 2010): 0. doi: 10.1021/ja106207w
2011/08/11 11 2	J. T. Yates, C. T. Campbell. From the Cover: Surface Chemistry Special Feature: Surface chemistry: Key to control and advance myriad technologies, Proceedings of the National Academy of Sciences, (01 2011): 0. doi: 10.1073/pnas.1006671107
2011/08/11 11 4	Peter Maksymovych, Oleksandr Voznyy, Daniel B. Dougherty, Dan C. Sorescu, John T. Yates. Gold adatom as a key structural component in self-assembled monolayers of organosulfur molecules on Au(111), Progress in Surface Science, (05 2010): 0. doi: 10.1016/j.progsurf.2010.05.001

**TOTAL: 3**

**Number of Papers published in non peer-reviewed journals:**

---

### **(c) Presentations**

- Nanotechnology for Defense, Atlanta, GA
- US- Egypt Advanced Studies Institute, Cairo
- ACS Meeting, San Francisco
- U. Calif. - Santa Barbara, Santa Barbara, CA
- Nanoscale Advisory Board, Manhattan, KS
- Materials Science and Engineering, Univ. Virginia
- Material Science Class-Professor C. Fraser
- U. Texas- San Antonio, TX
- University of California- Santa Barbara, CA
- ACS- Anaheim, CA
- PCSI-37, San Diego, CA
- U. Tennessee- Haines- Morris Lecture
- Oak Ridge National Laboratory- Discovery Lecture
- Materials Research Society, San Francisco, CA
- Georgia Tech- Atlanta, GA
- Emory U. - Atlanta, GA
- Georgia Tech- Chemical Physics
- MRS- San Francisco
- Bunsen Colloquium- Heidelberg
- Erlangen University- Material Science
- ACS- San Diego
- Krakow Physical Society- Poland
- DIET XIII-Stratford-on-Avon-UK
- ACS- Philadelphia
- Reactive-Chemical Systems-ARO- Providence, RI
- Virginia Commonwealth University-Physics,Richmond
- American Vacuum Society- Tampa, Florida ( Ana Stevanovic)
- International Clusters and Nanostructures, Richmond (Ana Stevanovic)

**Number of Presentations: 28.00**

---

### **Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
-----------------	--------------

**TOTAL:**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

Received

Paper

**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

---

**(d) Manuscripts**

Received

Paper

2011/08/11 11:55 Ana Stevanovic, Michael Buettner, Zhen Zhang, John T. Yates, Jr.. Photoluminescence of TiO<sub>2</sub>- Effect of UV Light and Adsorbed Molecules on Surface Band Bending, J. Am. Chem. Soc. (08 2011)

**TOTAL: 1**

Number of Manuscripts:

---

**Books**

Received

Paper

**TOTAL:**

**Patents Submitted**

---

**Patents Awarded**

---

**Awards**

J.T Yates Honors and Awards:

---

ACS Fellow 2011

T.E Madey Lecturer-Poland, 2012

Associate Editor Chemical Reviews, 2012

Ana Stevanovic:

AVS Mid Atlantic Chapter DC Regional Meeting at Jefferson Lab (2nd Place in Poster Session, 2012

AVS Mid Atlantic Chapter DC Regional Meeting at NIST (1st Place in Poster Session), 2011

---

**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	<u>Discipline</u>
Ana Stevanovic	1.00	
<b>FTE Equivalent:</b>	<b>1.00</b>	
<b>Total Number:</b>	<b>1</b>	

---

**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Zhen Zhang	0.30
<b>FTE Equivalent:</b>	<b>0.30</b>
<b>Total Number:</b>	<b>1</b>

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: .....	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense .....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: .....	0.00

### Names of Personnel receiving masters degrees

NAME

**Total Number:**

### Names of personnel receiving PHDs

NAME

**Total Number:**

### Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

**FTE Equivalent:**

**Total Number:**

---

**Sub Contractors (DD882)**

**Inventions (DD882)**

**Scientific Progress**

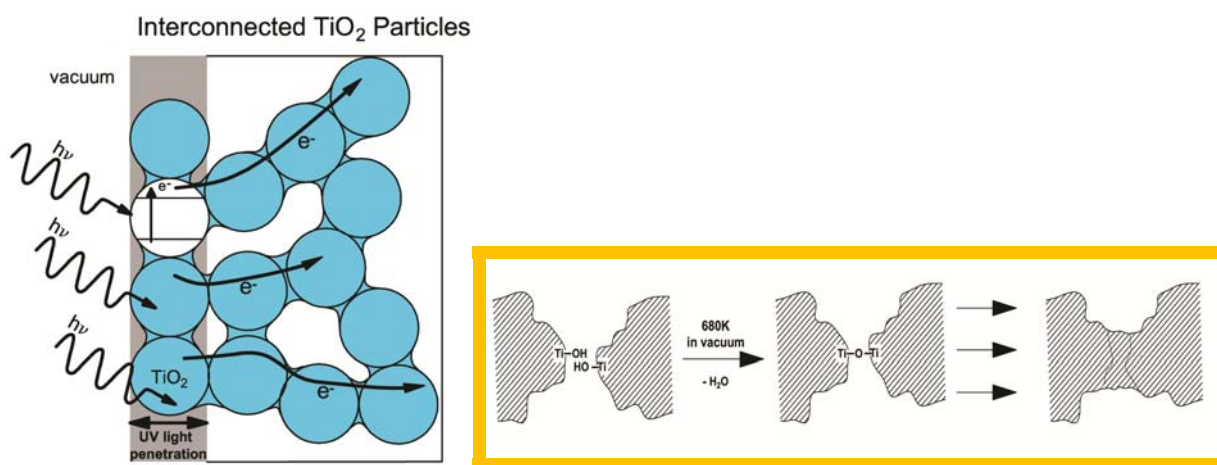
**Technology Transfer**

## Summary of Results- ARO Supported Research- 2010-2012

The main focus of our research has been to build and utilize a combined photoluminescence-IR spectroscopy apparatus (PL-IR) now being used in the study of particulate  $\text{TiO}_2$ - a material of great technological interest in the field of photovoltaics as well as in solar-driven decontamination strategies of interest to the military. This effort has been successful and two papers have been published using the new spectrometer-system. Two more papers are in the final stage of preparation. The spectrometer is unique in the world for its combination of the two surface spectroscopies, permitting the chemical and electronic behavior of particulate surfaces to be studied together. A second major accomplishment is the publication of an extensive review concerned with band bending on semiconductors entitled "Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces." This massive review has received a strong reception from the scientific community where in the first 30 days it has been the third most-viewed paper in Chemical Reviews. This follows up on the very high total citation count for three other ARO-supported reviews from my group concerned with  $\text{TiO}_2$  photochemistry [A. Linsebigler, et al., Chemical Reviews 95, 735 (1995)- **5,373 citations**; T. Thompson et al., Chemical Reviews 106, 48 (2006)- **731 citations**; and Surface Science, J.T. Yates, Jr. Surface Science 603, 1605 (2009)- **59 citations**. In addition, other studies of the behavior of self-assembled layers on gold surfaces have been pursued with partial assistance from ARO.

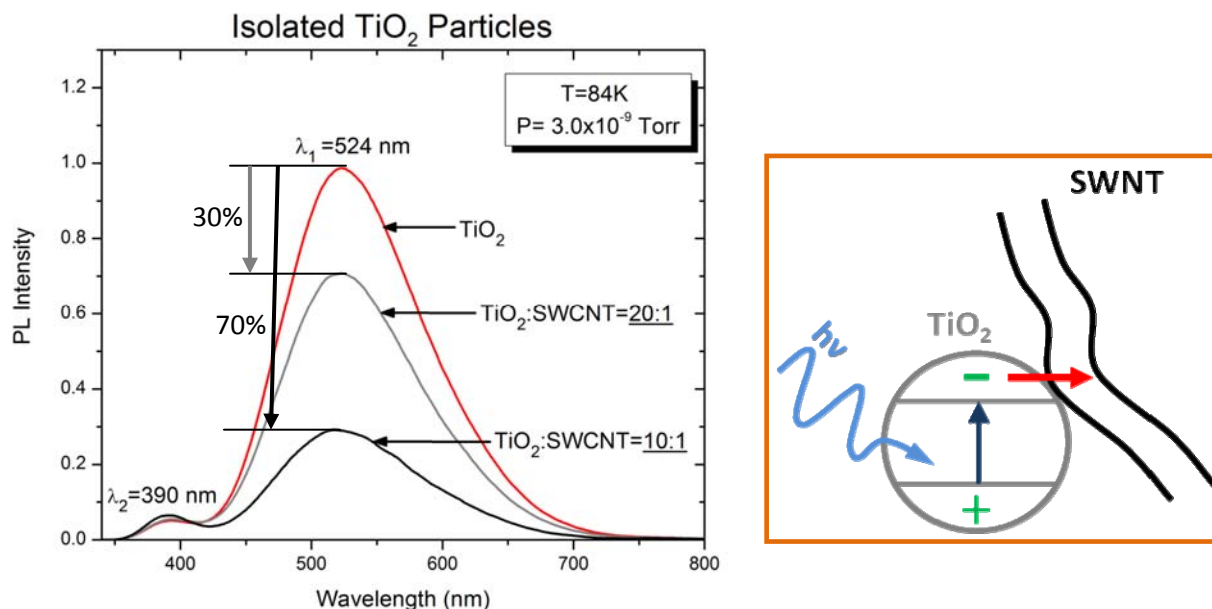
Below are described the details of the work accomplished to date under ARO support. In this work we have explored the use of PL spectroscopy for observing the effect of adsorption on band bending in particulate  $\text{TiO}_2$ . The new instrument permits us to probe the very outermost  $\text{TiO}_2$  particle in a packed bed of particles. We can see at very high sensitivity the progress of adsorption from the outermost parts of the particle bed to the interior- an effect which is very important in optimizing the efficiency of sorbents and detectors involving powdered active material. The PL method also allows charge transfer effects to be

spectroscopically witnessed by following the effect of UV irradiation on the surface potential of the  $\text{TiO}_2$  particles. A build up of surface photovoltage is observed when the particles are disconnected from each other. Upon connection of the particles using a very simple hydrolysis method which we have devised (see Figure 1), surface photovoltage is dissipated by carrier conduction through a network of interconnected  $\text{TiO}_2$  particles and this may be readily observed by the PL behavior.



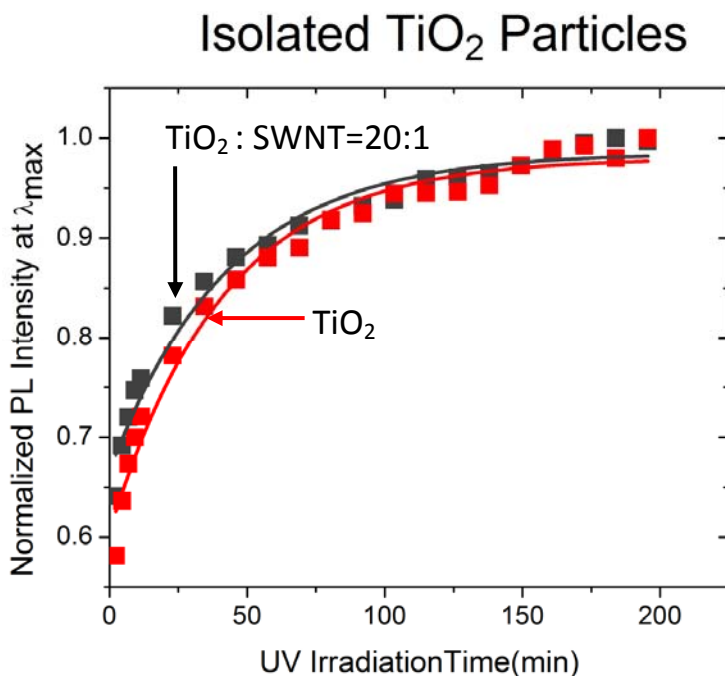
**Figure 1. Interconnected  $\text{TiO}_2$  particles made by hydrolysis.**

Two publications are being written. One is concerned with the interaction of single walled nanotubes (SWNTs) with  $\text{TiO}_2$  when irradiated by UV light. As expected, SWNTs are good acceptor molecules, decreasing photoluminescence when mixed with  $\text{TiO}_2$  as shown in Figure 2.



**Figure 2. Effect of Mixed SWNT-  $\text{TiO}_2$  on Photoluminescence.**

A second publication in preparation concerns the ability of SWNTs to conduct charge between  $\text{TiO}_2$  particles- a favorite proposed use of SWNTs. Here we see that inter-particle conductivity is not enhanced by SWNTs as measured by the very similar rate of charge buildup in isolated and in SWNT-connected particles as shown in Figure 3. The reason for this effect could be charge recombination at defects in the SWNTs and this will be further investigated. Other methods of enhancing interparticle conductivity will be explored such as the use of volatile linker molecules and the use of gold connector particles, as proposed in a new proposal under consideration by ARO.



**Figure 3. Lack of TiO<sub>2</sub> Inter-particle Conductivity Caused by SWNTs**

**Published work:**

**1. Probe of NH<sub>3</sub> and CO Adsorption on the Very Outermost Surface of a Porous TiO<sub>2</sub> Adsorbent Using Photoluminescence Spectroscopy**

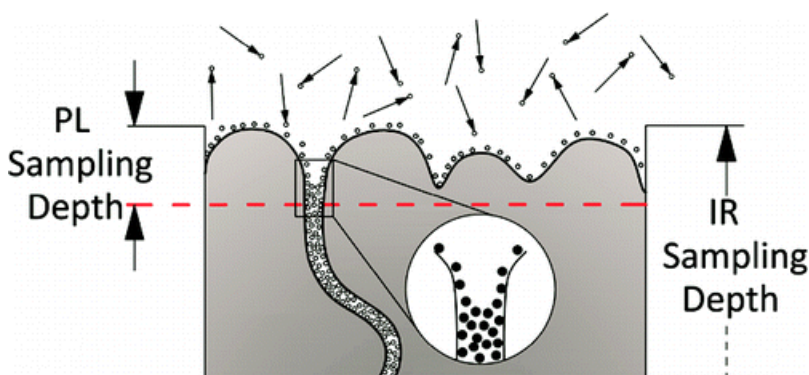
**Ana Stevanovic and John T. Yates, Jr.\***

**Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904,  
United States**

***Langmuir*, 2012, 28 (13), pp 5652–5659**

We report the first measurements of the kinetics of adsorption on the very outermost surface sites of a porous material compared to measurements made of adsorption on the interior sites. NH<sub>3</sub> and CO were employed in this study as representative of slow diffusion and fast diffusion, respectively, through porous TiO<sub>2</sub>. Adsorption of NH<sub>3</sub> at 200 K occurs mainly at the very near surface (~20 nm) region as observed by photoluminescence (PL) spectroscopy, and its distribution by surface diffusion through the powder is highly retarded as judged by transmission IR spectroscopy. In contrast, the adsorption of CO in the near-

surface region at 120 K is followed by the fast distribution of CO by surface diffusion into TiO<sub>2</sub> powder, causing the near-surface CO coverage to lag behind the coverage in the bulk. In the desorption process, the near-surface region delivers adsorbed CO molecules into the gas phase, accompanied by the supply of diffusing CO molecules from the interior. As a result, the adsorption/desorption processes for CO in the near-surface region of porous TiO<sub>2</sub> show a pronounced hysteresis effect. As surface diffusion is retarded at lower temperatures, the hysteresis effect gradually disappears.

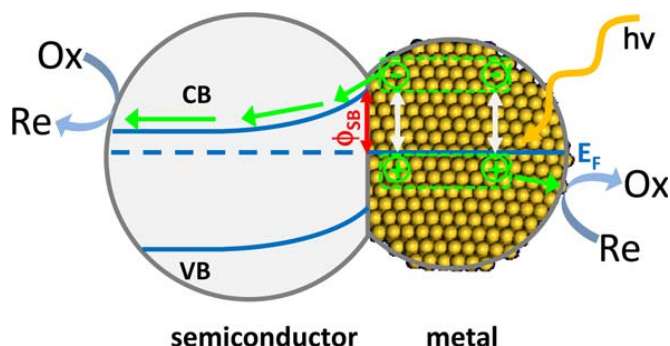


## 2. Band Bending in Semiconductors: Chemical and Physical Consequences at Surfaces and Interfaces

Zhen Zhang and John T. Yates , Jr.\*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States  
*Chem. Rev.*, 2012, 112 (10), pp 5520–5551

Band bending at semiconductor surfaces is a phenomenon with widespread applications in areas of surface photochemistry, junction phenomena in electronics, heterogeneous catalysis, photovoltaics and electrochemistry. This comprehensive review concerns the origin of band bending, how band bending is measured, and its influence on charge transfer at surfaces. Surface science methods now permit band bending to be measured in a local fashion and allow one to manipulate band bending in a number of informative ways to govern the behavior of electronic devices.



### 3. Electron stimulated desorption, DIET, and photochemistry at surfaces: A personal recollection

John T. Yates, Jr.

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, USA  
J. Chem. Phys. 137, 091701 (2012);

This personal recollection describes my involvement with others in the beginning of the fields of electron stimulated desorption, desorption induced by electronic transitions (DIET), and photochemistry on surfaces. ARO had much to do with our beginning work on surface photochemistry, where work on  $\text{TiO}_2$  surfaces was supported.

The photochemistry on  $\text{TiO}_2$  is connected to many military technologies such as the destruction of chemical agents by sunlight, the improvement of photovoltaic cells and the development of sensors related to the electronic excitation of semiconductors. The topic of photochemistry at surfaces constitutes a major portion of the field of surface science today.

### 4. The Role of Gold Adatoms and Stereochemistry in Self-Assembly of Methylthiolate on Au(111)

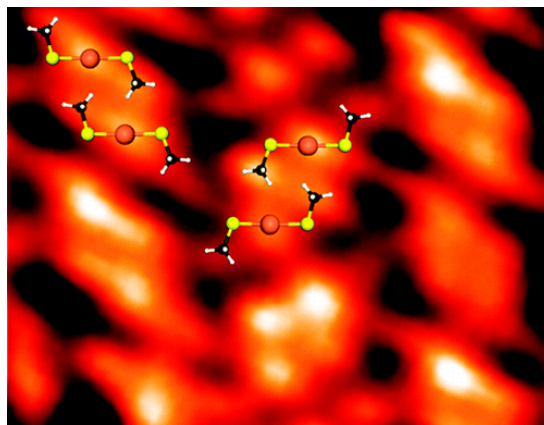
Oleksandr Voznyy<sup>†</sup>, Jan J. Dubowski<sup>†</sup>, J. T. Yates, Jr.<sup>‡§</sup> and Peter Maksymovych<sup>§||</sup>

Department of Electrical and Computer Engineering, Centre of Excellence for Information Engineering (CEGI), Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada, Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania

15217, and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory,  
Oak Ridge, Tennessee 37831

*J. Am. Chem. Soc.*, 2009, 131 (36), pp 12989–12993

On the basis of high resolution STM images and DFT modeling, we have resolved low- and high-coverage structures of methylthiolate ( $\text{CH}_3\text{S}$ ) self-assembled on the Au(111) surface. The key new finding is that the building block of all these structures has the same stoichiometry of two thiolate species joined by a gold adatom. The self-arrangement of the methylthiolate–adatom complexes on the surface depends critically on their stereochemical properties. Variations of the latter can produce local ordering of adatom complexes with either  $(3 \times 4)$  or  $(3 \times 4\sqrt{3})$  periodicity. A possible structural connection between the  $(3 \times 4\sqrt{3})$  structure and commonly observed  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase in methylthiolate self-assembled monolayers is developed by taking into account the reduction in the long-range order and stereochemical isomerization at high coverage. We also suggest how the observed self-arrangements of methylthiolate may be related to the  $c(4 \times 2)$  phase of its longer homologues.



## 5. Photoluminescence of $\text{TiO}_2$ : Effect of UV Light and Adsorbed Molecules on Surface Band Structure

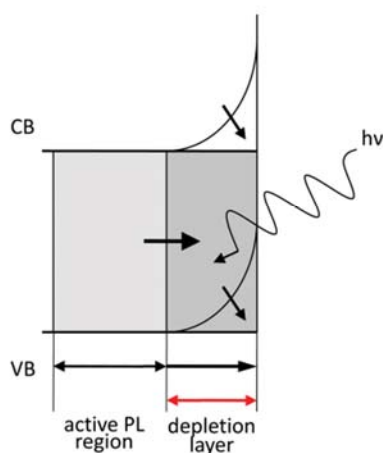
Ana Stevanovic, Michael Büttner, Zhen Zhang, and John T. Yates, Jr.

*J. Am. Chem. Soc.*, 2012, 134 (1), pp 324–332

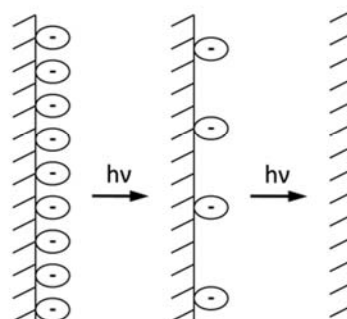
The photoluminescence (PL) of  $\text{TiO}_2$  at 529.5 nm (2.34 eV) has been found to be a sensitive indicator of UV-induced band structure modification. As UV irradiation

occurs, the positive surface potential changes and shifts the depth of the depletion layer. In addition, reversible band bending due to the adsorption of the electron-donor  $\text{NH}_3$  and  $\text{CO}$  molecules has been observed in measurements combining PL with FTIR surface spectroscopy. It has been found that the  $\text{O}_2$  molecule acts in two ways: as a reversibly adsorbed electron-acceptor molecule and as an irreversibly adsorbed molecule that heals natural oxygen vacancy defects in the near-surface region.

**A. Enhancement of Active PL Region**



**B. Change of Surface Charge Distribution**



## 6. Electron-Mediated CO Oxidation on the $\text{TiO}_2(110)$ Surface during Electronic Excitation

Zhen Zhang and John T. Yates, Jr.\*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904

*J. Am. Chem. Soc.*, 2010, 132 (37), pp 12804–12807

The role of electrons and holes in the electronically excited oxidation of adsorbed  $\text{CO}$  on  $\text{TiO}_2(110)$  has been investigated by tuning the surface electron and hole availability by the adsorption of  $\text{Cl}_2$  or  $\text{O}_2$ . The presence of an electron acceptor ( $\text{Cl}_2$  or  $\text{O}_2$ ) on the  $\text{TiO}_2(110)$  surface causes upward band bending, increasing the excited hole availability and decreasing the excited electron availability in the near surface region. This enhances  $\text{O}_2$  desorption and depresses  $\text{CO}_2$  production during electronic excitation. This result gives clear evidence for the first time that

the electronically excited CO oxidation reaction is caused by an electron-mediated process in contrast to O<sub>2</sub> desorption which is mediated by holes.

**Schematic Mechanism of Electron- and Hole-Driven Surface Processes on TiO<sub>2</sub>(110)**

